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EFFECT OF NON-UNIFORM TEMPERATURE DISTRIBUTION
ON ACID HYDROLYSIS OF ASPEN HEMICELLULOSE

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ABSTRACT

The thermal diffusivities of Aspen wood were experimentally determined. The data were incorporated into a theoretical model designed to study the effect of transient temperature variation within the solid substrate during acid catalyzed hydrolysis of hemicellulose (prehydrolysis). The kinetic and the modelling results were analyzed to assess the effect of particle size on acid hydrolysis of hemicellulose. Among the important findings was that as the chip size increases, the maximum attainable yield of xylose decreases and the reaction time at which the maximum yield occurs increases. This effect becomes more significant as the temperature and the acid level increases. Quantitative criteria were therefore established to show the effect of particle size on the yield and the reaction time at various reaction conditions.

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INTRODUCTION

Selective hydrolysis of hemicellulose from cellulosic biomass is a necessary component in the integral biomass conversion process. Various aspects of this process have been investigated including the kinetics, reactor design, and diffusion related problems (1-4,9,10). In most of the previous studies the reaction has been viewed as an isothermal reaction. However, it is an assumption that is not always justifiable from the following considerations.

In a typical acid hydrolysis process, whether it is cellulose or hemicellulose, the cellulosic substrate is presoaked with sulfuric acid, then exposed to steam for rapid heating. During this transient heating period, the temperature within the biomass structure changes rather drastically; initially at uniform low temperature, to high temperature at the outer surface and low temperature at the center region, eventually to uniform high temperature. Such a temperature variation creates a fundamental and unique problem concerning heterogeneous reaction engineering since it alters the reaction progress from that expected if the reaction is isothermal throughout. Whether this transient variation of temperature significantly affects the overall reaction depends chiefly on the relative rate of reaction to conduction. For example, if the conduction is extremely fast compared to the reaction, an isothermal temperature profile would be quickly established within the solid substrate. The extent of the reaction occurring during the preheating period would then be negligible, justifying the isothermal assumption. Conversely, if the reaction is much faster than the conduction, most of the reaction would occur during the preheating period. Since the rate of reaction and the rate of conduction strongly depend on the reaction condition and the size of the solid feed respectively, these two parameters become the key factors in this problem. This non-uniform temperature distribution in essence signifies the effect of biomass size on the hydrolysis reaction. Since size reduction is a cost intensive unit process, it is a potential economic issue as well as a technical problem (5,7).

This study was undertaken to set up a quantitative criteria concerning the size of the biomass; what degree of size reduction for biomass feed is required to prevent loss of sugar yield in prehydrolysis of hardwood hemicellulose for a given reaction condition.

EXPERIMENTAL METHODS

Thermal Diffusivity Measurement

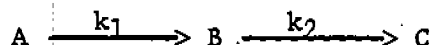
The thermal diffusivity ($\alpha = k/\rho C_p$) of the Aspen wood sample was determined experimentally by a dynamic method. In the experimental procedure, a thermocouple was inserted into the center point of the wood sample. Upon heating the sample, the variation of the centerpoint temperature was traced and recorded into a data logging computer (IBM PC/XT). Sigma thermocouple thermometer (2175A), a signal amplifier/offset unit, IBM data acquisition and control board were incorporated into the experimental setup as described in

Fig. 1. The samples were cut into a cylinder form with a dimension of 6 to 1 in diameter to height ratio. The circular surface of the sample was insulated with silicone rubber forcing unidirectional heat flow. Two different wood samples were prepared; one to take the data for heat conduction in longitudinal direction of wood (parallel to grain), and the other for radial direction (perpendicular to grain). The actual data on variation of temperature with time at the center of the wood chip sample are shown in Fig. 2. The temperature data were then statistically analyzed using SAS non-linear algorithm (available from Auburn University IBM main frame) to determine the thermal diffusivity value. This statistical parameter estimation was done in conjunction with the analytical solution for one dimensional unsteady state conduction equation provided in the next section.

RESULTS AND DISCUSSION

Kinetics

Literature information pertaining to the kinetics of acid catalyzed hydrolysis of hemicellulose is abundant (1-4,9,10). However these literature kinetic data have shown significant disparity among themselves due to the kinetic dependence on the species of substrate, method of pretreatment, and the reaction conditions. For this study, we have chosen the recent kinetic data determined specifically for Aspen wood by Brennan et.al.(3) to be used for this study. The hydrolysis reaction was modelled as a consecutive first order reactions:



The rate constants k_1 , k_2 were expressed by Arrhenius equation with the addition of an added acid term as follows:

$$k_i = k_{i0} H^{n_i} e^{-E_i/RT} \quad (1)$$

where H is the acid concentration (in wt.%). The six parameters which characterize the rate constants k_1 and k_2 as determined by Brennan et. al.(3) are as follows:

i	k_{i0} (min. ⁻¹)	n_i	E_i (cal/mol)
1	6.17×10^{13}	1.17	27827
2	2.33×10^{12}	0.69	27130

Effect of Particle Size

Model Development. In addition to the kinetic data, three major steps (heat balance, thermal diffusivity determination, and material balance) were taken in studying the effect of particle size on acid hydrolysis of Aspen hemicellulose.

First, a heat balance within a differential segment of the chip results an unsteady state conduction equation,

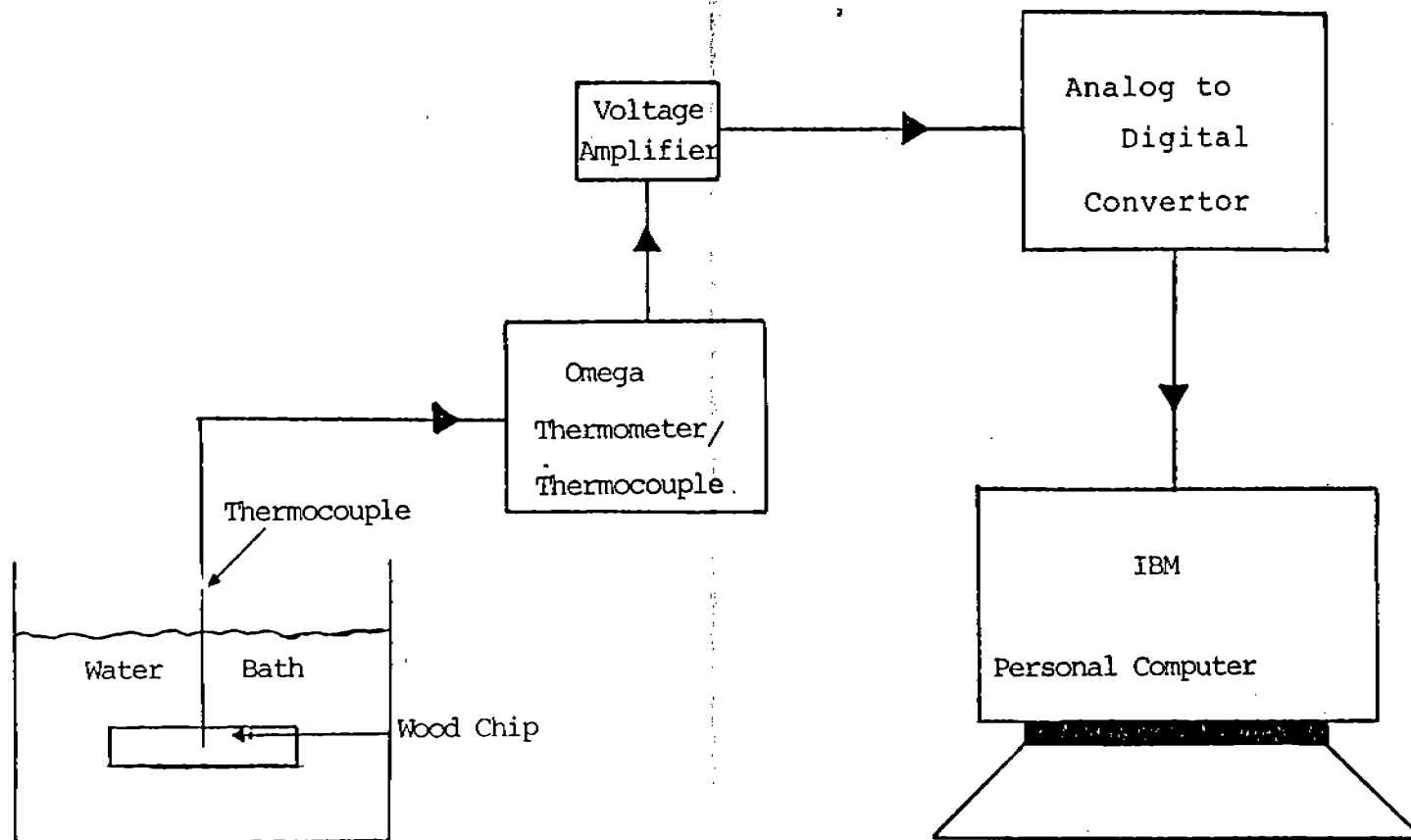


Figure 1. Schematic of the experimental setup for measurement of thermal diffusivity of wood

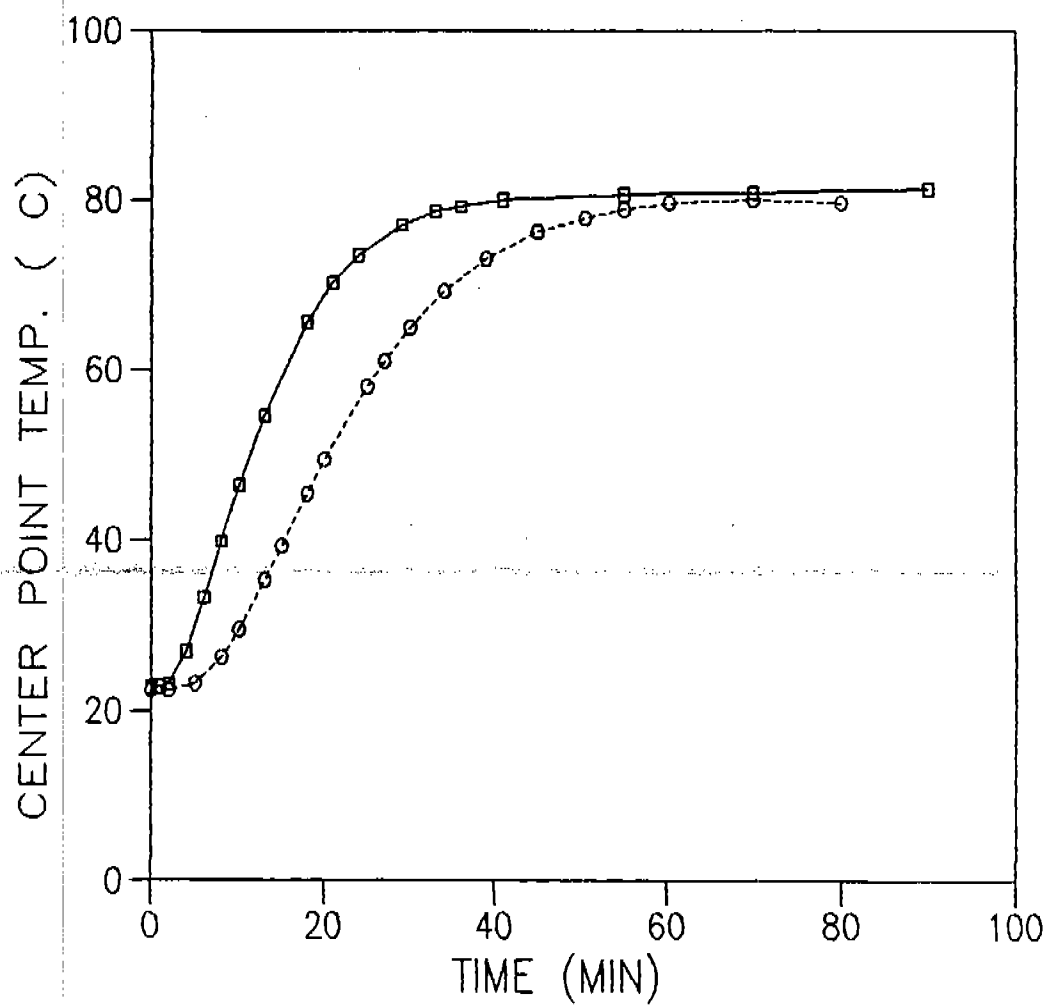


Figure 2. Actual temperature profile at the center of wood chip in thermal diffusivity experiment, $L = 2.0$ cm, \square :longitudinal, \circ :radial

$$\frac{\delta T}{\delta t} = \alpha \frac{\delta^2 T}{\delta x^2} \quad (2)$$

with the boundary and initial conditions of

$$x = 0, \quad \frac{\delta T}{\delta x} = 0 \quad (3)$$

$$x = L, \quad -k \frac{\delta T}{\delta x} = h(T - T_s) \quad (4)$$

$$t = 0, \quad T = T_o \quad (5)$$

The analytical solution to Eq. (2)-(5) is obtained in the dimensionless form as follows.

$$\Psi = \sum_{n=0}^{\infty} \frac{2Nu(Nu^2 + \lambda_n^2)^{-\frac{1}{2}}}{\lambda_n(Nu^2 + \lambda_n^2 + Nu)} \exp(-\lambda_n^2 \tau) \cdot \cos(\lambda_n z) \quad (6)$$

where $\tau = \alpha t/L^2$, $z = x/L$, $\Psi = (T - T_s)/(T_o - T_s)$, $Nu = hL/k$ and

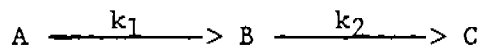
$$\lambda_n \tan \lambda_n = Nu, \quad \lambda_n > 0 \quad (7)$$

Although this classical solution can be found in various heat transfer textbooks, it is also graphically presented in Fig. 3 since it plays an important role in the subsequent analyses dealing with thermal diffusivity and the non-isothermal reaction. During the computation, it was found that the Nu based on the heat transfer coefficient for condensing steam (6,8) gave large enough value that it had no effect on the outcome, making the solution essentially same as that with a boundary condition of $T = T_s$ at $x = L$.

Thermal Diffusivity Determination. The thermal diffusivities of Aspen wood presoaked with water were determined by subjecting the experimental data to Eq. (6). The procedure involved a computer aided calculation in which a best fit thermal diffusivity value (lumped into the dimensionless time, $\tau = \alpha t/L^2$) was determined by a statistical parameter estimation algorithm.

The thermal diffusivities in the longitudinal and radial directions were found to be $(2.33 + 0.052) \times 10^{-7} \text{ m}^2/\text{s}$ and $(1.72 + 0.048) \times 10^{-7} \text{ m}^2/\text{s}$ respectively. The error intervals are for 95% confidence level. These values were in close proximity with a literature value reported for hardwood (11). The wood chips are usually cut in random direction. Therefore the values of the thermal diffusivities (of hemicellulose-free wood) determined for the two different directions were averaged into $2.03 \times 10^{-7} \text{ m}^2/\text{s}$ and used in subsequent calculations.

Material Balance. The thermal situation represented by Eq. (6) along with experimentally determined thermal diffusivity were incorporated into the computation of the chemical reaction occurring inside the wood chip with varying temperature profile. It is important to note that for the reaction scheme,



the rate constants of k_1 and k_2 are function of temperature, therefore function

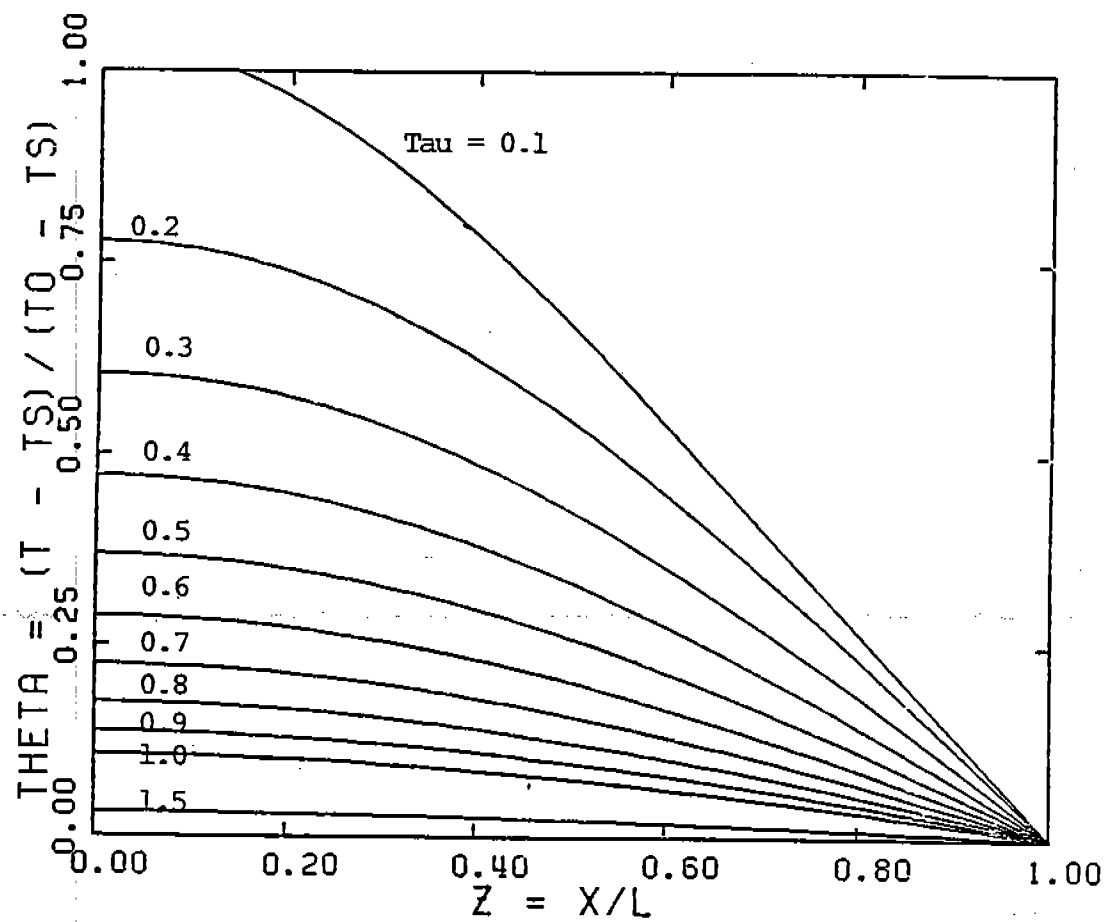


Figure 3. Unsteady-state temperature variation in a slab

of position within wood chip and reaction time such that

$$\begin{aligned}k_1 &= k_1(T) = k_1(t, x) \\k_2 &= k_2(T) = k_2(t, x)\end{aligned}$$

The reaction progress in wood chip is described by

$$-\frac{dC_A}{dt} = k_1 C_A \quad (8)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (9)$$

with initial conditions of

$$C_A = C_{A0} \text{ and } C_B = C_{B0} \text{ @ } t = 0 \quad (10)$$

These equations were put into dimensionless forms and solved numerically. The computer program was set up such that it first evaluates the temperature at particular values of r and z . It then evaluates the rate constants k_1 and k_2 at that temperature using the values of the kinetic parameters determined in the previous section. With known k_1 and k_2 , Range-Cadet fourth order method was employed to solve the two initial value problems of Eq. (8)-(10). Simpson's rule was then applied to evaluate xylose concentration (C_B) at any time by integrating over the length of the chip. Sample results of the computation are shown in Fig. 4 and 5 representing two of the various conditions studied.

It is clear from these figures that as the chip size increases, the maximum yield of xylose decreases (loss of yield) and the reaction time at which the maximum occurs increases (delay in reaction). It is also noticeable that as the chip size increases, the delaying effect is seen first before loss of yield occurs. These effects are obviously caused by the variation of temperature across the chip. One can visualize this situation as follows. At the initial stage of the reaction, the rate of hydrolysis is higher at the surface and it decreases near the center. However, as time progresses, the hydrolysis reaction zone moves toward the center while sugar decomposition occurs near the surface. The net effect of this is lower yields and longer reaction times than those expected from isothermal condition.

The graphical data clearly indicate that the effect of particle size (non-uniform temperature distribution) becomes significantly greater as the reaction conditions (acid concentration and/or reaction temperature) become stronger. Table 1 contains the summary of the results. In the table, the maximum xylose yield and reaction time at which maximum yield occurs are listed for various reaction conditions and chip sizes. These values were normalized such that value of one indicates no effect of temperature distribution. The criteria concerning the effect of particle size can be set from the table for each experimental condition. For example, at 167°C and 1.0% H_2SO_4 , the effect of non-uniform temperature distribution on the reaction time becomes significant for chip thickness of 0.2 cm (or $L=0.1$ cm), whereas the effect on the yield is not shown until the size reaches 1.50 cm (or $L=0.75$ cm). The results contained in this table would serve as a useful guide for feed preparation, reactor design, and operation strategy.

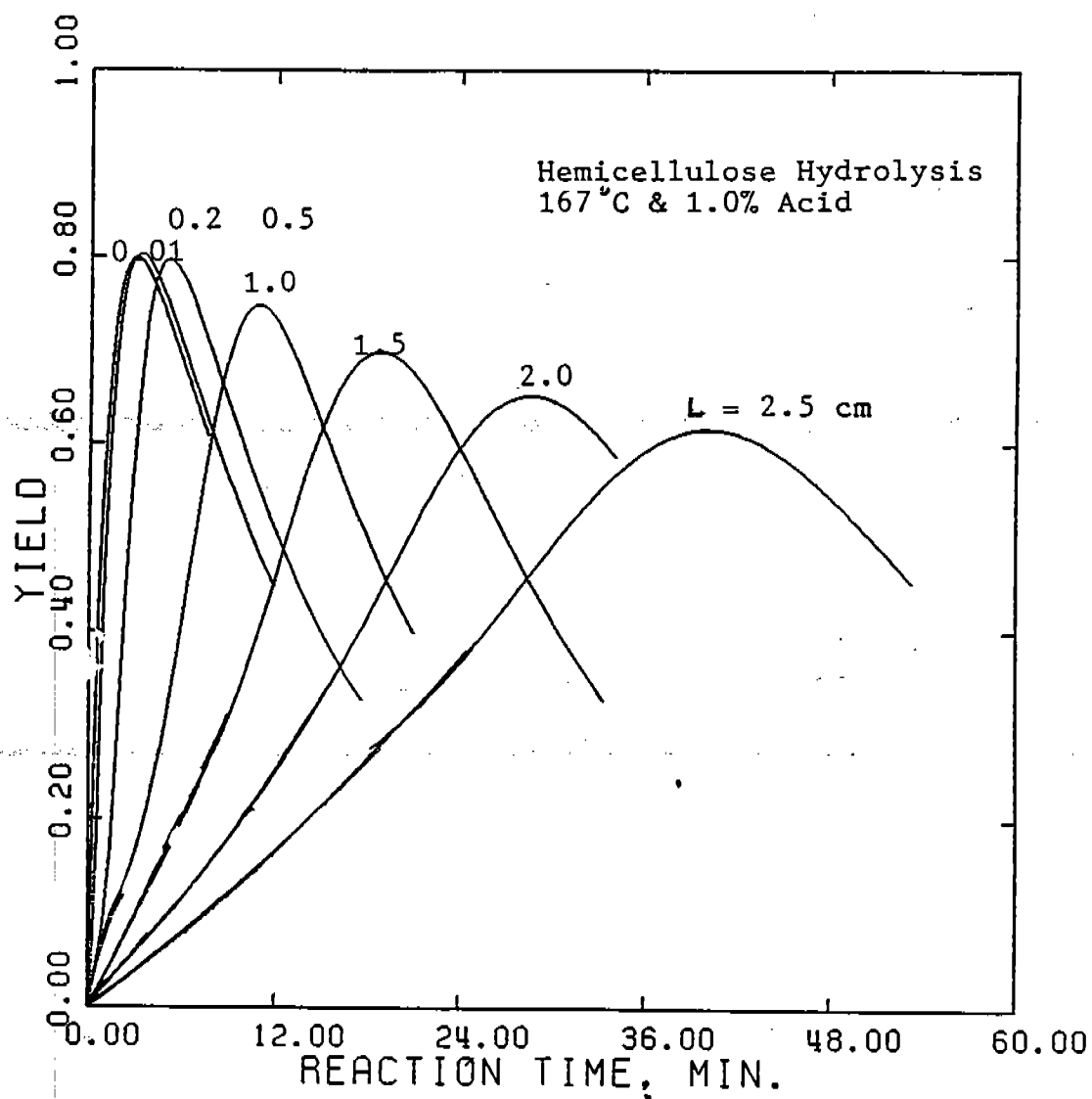


Figure 4. Effect of chip size on xylose yield and reaction time at 167°C and 1.0% H_2SO_4

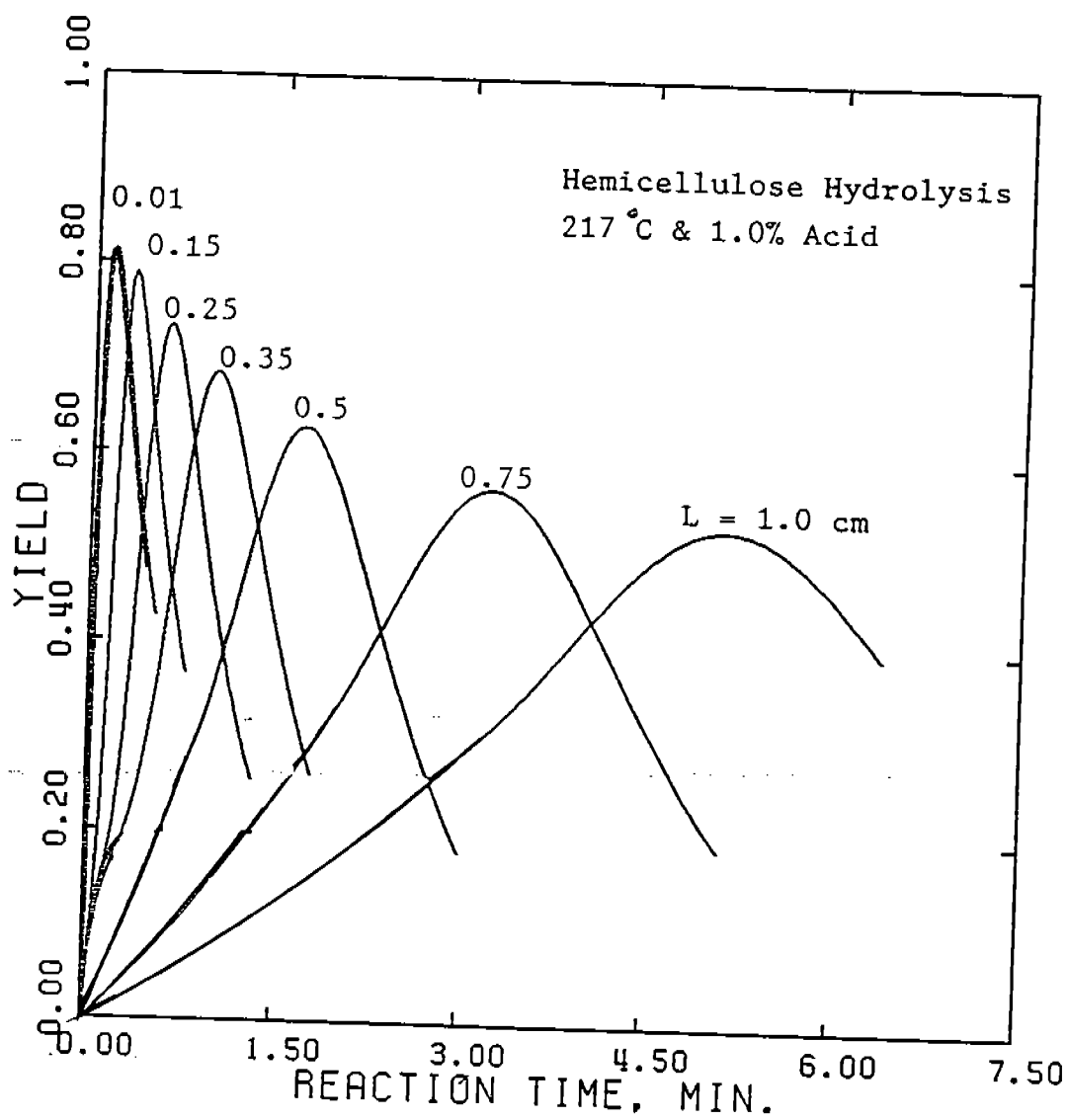


Figure 5. Effect of chip size on xylose yield and reaction time at 217°C and 1.0% H₂SO₄

Table 1

Comparison of Maximum Yield and Reaction Time
for Various Chip Sizes in Hydrolysis of Aspen Hemicellulose

Conditions	167°C, 1.0%		217°C, 1.0%		255°C, 1.0%	
	a	b	a	b	a	b
Uniform temp.	1.00	1.000	1.00	1.000	1.00	1.000
0.01 cm	1.00	1.000	1.00	1.000	1.07	1.000
0.05 cm	1.01	1.000	1.26	1.000	2.47	0.970
0.10 cm	1.03	1.000	1.87	0.989	6.13	0.890
0.15 cm	1.08	1.000	2.61	0.972	11.13	0.815
0.20 cm	1.11	1.000	3.87	0.953	17.50	0.760
0.25 cm	1.19	1.000	5.08	0.904	25.00	0.714
0.35 cm	1.38	1.000	8.34	0.842	---	---
0.50 cm	1.76	1.000	14.41	0.773	---	---
0.75 cm	2.43	0.963	27.84	0.695	---	---
1.00 cm	3.71	0.940	43.19	0.648	---	---
1.50 cm	6.47	0.876	---	---	---	---
2.00 cm	9.83	0.810	---	---	---	---
2.50 cm	13.80	0.770	---	---	---	---

a - $\frac{\text{Reaction time with uniform temperature}}{\text{Reaction time}}$

b - $\frac{\text{Maximum yield}}{\text{Maximum yield with uniform temperature}}$

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Notations

A = hemicellulose (xylan)
B = xylose
C = decomposition products
 C_i = concentration
 k_i = first order rate constant
i = reaction index (1 for hydrolysis and 2 for decomposition)
 k_{i0} = frequency factor
H = % acid concentration
 n_i = acid exponent
 E_i = activation energy
R = gas constant
T = absolute temperature
t = reaction time
x = position in a slab measured from the center
z = x/L
 T_s = steam temperature
 T_0 = initial temperature
k = thermal conductivity
h = heat transfer coefficient
L = half of the thickness of a slab
 $Nu = hL/k$ = Nusselt number
 $\alpha = k/\rho C_p$ = thermal diffusivity
 λ_n = eigen values defined by Eq. (7)
 Ψ = dimensionless temperature = $(T - T_s)/(T_0 - T_s)$
 τ = dimension less time = $\alpha t/L^2$

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CELL WALL MECHANISMS OF RESISTANCE TO ENZYMATIC HYDROLYSIS

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ABSTRACT

As isolated polymers, celluloses are readily hydrolyzed by acids or cellulolytic enzymes to yield glucose, although only acids can readily access and hydrolyze cellulose in lignocellulose, the lignified cell wall substance of plants.

This research concerns mechanisms of plant cell wall resistance to attack by polysaccharide degrading enzymes, and more specifically a determination of the relative roles of hemicellulose (xylan) and lignin in the cellulose accessibility issue. The overall working hypothesis of this research effort is that topochemical considerations in fibrillar structure as well as hemicellulose content and orientation have not been fully credited for the resistance of lignified tissues to enzymatic hydrolysis.

Initial research objectives are to:

- (1) develop a mild, chlorine dioxide-based, holocellulose procedure for aspen wood and wheat straw, which will produce research materials retaining as much as possible of the original hemicellulose of the parent substrates in chemically unaltered form; and,
- (2) subject the various prepared holocelluloses to cellulase/ hemicellulase digestibility studies for preliminary assessment of the relative roles of hemicellulose and lignin in resistance of plant cell walls to enzymatic attack.